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Effect of polymerization protocol on the degree of conversion of photo- and dual-polymerized self-etch adhesives

**Lamiaa Mohmoud Moharam, BDS, MSc, PhD^a / Sara Adel Botros, BDS, MSc^b /
Farid Sabry El-Askary, BDS, MSc, DDS^c / Mutlu Özcan, Dr.med.dent., PhD^d**

^aResearcher, Restorative and Dental Materials Department, National Research Center, Giza, Egypt

^bMaster`s Degree Student, Operative Dentistry Department, Faculty of Dentistry, Ain Shams University, Cairo, Egypt

^cProfessor, Operative Dentistry Department, Faculty of Dentistry, Ain Shams University, Cairo, Egypt

^dProfessor, University of Zurich, Dental Materials Unit, Center for Dental and Oral Medicine, Clinic for Fixed and Removable Prosthodontics and Dental Materials Science, Zurich, Switzerland

Short title: *Effect of adhesives and polymerization protocols on degree of conversion*

Correspondance to: *Prof. Dr. med. dent. Mutlu Özcan, University of Zürich, Dental Materials Unit, Center for Dental and Oral Medicine Clinic for Fixed and Removable Prosthodontics and Dental Materials Science, Plattenstrasse 11, CH-8032, Zürich, Switzerland. Tel: +41-44-63 45600, Fax: +41-44-63 44305. e-mail: mutluozcan@hotmail.com*

Abstract: This study investigated the effect of different polymerization protocols on the degree of conversion (DC%) of various photo-polymerized and dual-polymerized self-etch adhesive resins. Five different photo-polymerized (All-Bond Universal, Bisco; G-ænial Bond, GC; Futurabond M+ LC, VOCO; Single Bond Universal LC, 3M ESPE and Peak Universal Bond, Ultradent) and four dual-polymerized self-etch adhesives (Futurabond U, VOCO; Gradia Core SE, GC; Futurabond M+ DC, VOCO and Single Bond Universal DC, 3M ESPE) were tested. All adhesives were applied on potassium bromide pellets (KBr) following the manufacturer's instructions. The KBr pellets were divided into 10 experimental groups for the photo-polymerized adhesives and 12 experimental groups for the dual-polymerized adhesives according to the two levels of the study, Level 1: Polymerization protocol and Level 2: Adhesive system. For the photo-polymerized adhesives, the adhesives were polymerized either at 1 mm or 10 mm from the KBr pellets. For the photo-polymerized adhesives, the adhesives were photo-polymerized either at 1 mm or 10 mm distance or polymerized chemically. The DC% of the unpolymerized and polymerized adhesives was assessed using Fourier transform infrared spectroscopy (FTIR). Data were analyzed using two-Way ANOVA to evaluate the effect of polymerization protocol, adhesive system and their interaction on the DC% of the self-etch adhesives. For the photo-polymerized and dual-polymerized adhesives, one-Way ANOVA and Tukey HSD post hoc test was used to evaluate the effect of adhesive system within each polymerization protocol and the effect of polymerization protocol within each adhesive for the dual-polymerized adhesives ($p=0.05$). Student t-test was used to compare the effect of polymerization distances within each photo-polymerized adhesive. For both photo- and dual-polymerized adhesives, the polymerization protocol and adhesive system had a significant effect on the DC ($p=0.000$). The interaction between the two factors (polymerization protocol and adhesive system) revealed also a significant effect on the DC% of the different

adhesives ($p=0.000$). Polymerization distance of 1 mm showed significantly higher DC% compared to 10 mm distance. When the dual-polymerized adhesives were left to set chemically, they showed the lowest DC% among all polymerization protocols. DC varied depending on the chemical composition of the self-etch adhesives. The tip of the polymerization device should be positioned as close as possible to the surface to achieve higher DC% of the tested adhesives. Photo-polymerization of the dual-polymerized self-etch adhesives is a mandatory step to improve their DC.

Keywords: Degree of conversion, dual-cure, photo-polymerization, self-etch adhesives

Introduction

Over the past few decades, the advances in dentin adhesive systems have extensively revolutionized the field of restorative dentistry. Dentin bonding agents have evolved through several generations with changes in their chemical formulations, mechanisms of action and number of application steps. Depending on the adhesion strategy, modern adhesive systems can be principally categorized into three major groups: etch-and-rinse, self-etch and glass-ionomer based adhesives [1,2]. Each group can be further classified according to the number of clinical application steps as three-step or two-step etch-and-rinse adhesives, and two-step or one-step self-etch adhesives [2].

Despite the long-term clinical success that has been achieved with etch-and-rinse adhesive systems, development of self-etch adhesives has been an appealing solution to simplify the clinical procedures without compromising the retention or adhesion of dental restorations [3-7]. Self-etch adhesive resins mainly rely on the use of acidic monomers that simultaneously demineralize and infiltrate into the tooth substrate, eliminating the need of a separate rinsing step, thereby forming a strong micromechanical bond [8,9]. By incorporating smear plugs into the resin tags, there is less potential for sensitivity as the dentinal tubules remain sealed to a great extent [10,11]. However, high concentration of acidic resin components in contemporary simplified adhesive resins increases their hydrophilicity and dramatically reduces their hydrolytic stability [12].

Simplified adhesive resins have been shown to act as semi-permeable membranes permitting water penetration through the resin-dentin interfaces [13,14], resulting in reduced bond durability [15-18]. Studies have reported that the permeability phenomenon could be attributed to the presence of incompletely polymerized acidic monomers within the hybrid layer or dentinal tubules [13,19,20]. Therefore, a low degree of conversion can be associated with increased water sorption, polymer

plasticization [21,22], high monomer elution [23] and continuous etching of the tooth substrate [24], resulting in compromised mechanical properties and low bond strength values. Moreover, the presence of unreacted acidic monomers have been found to inactivate the tertiary amines of self- and dual-polymerized composite resins, subsequently retarding their polymerization reaction [25]. Hence, obtaining high degrees of monomer conversion is essential for establishing a long-lasting bonded assembly [26].

Generally, the polymerization reaction of photo-activated adhesive resins requires a sufficient amount of energy to maintain camphorquinone, the photoinitiator, in an excited (triplet) state to generate free radicals that initiate polymerization [27]. In some clinical situations, the bonding agent might not be accessible to the polymerization unit. This could be encountered in cases of deep proximal boxes, where the gingival floor could be more than 8 mm away from the light source [28], or when using the adhesive resins in conjunction with resin cements during luting fiber posts. In such cases, the light intensity reaching the resinous material surface could be strongly attenuated, leading to decreased degree of conversion of the resin material, thereby impeding adequate polymerization [29-31].

The objectives of this study therefore, were to evaluate the effect of different polymerization protocols on the degree of conversion (DC%) of photo-polymerized self-etch adhesives and dual-polymerized self-etch adhesives. The null hypotheses to be tested were that the different polymerization protocols would not influence on the DC% of photo-polymerized self-etch adhesives and dual-polymerized self-etch adhesives.

Materials and Methods

The brands, abbreviations, manufacturers, chemical compositions, and batch numbers of the adhesive resins used for the experiments are listed in Table 1.

Nine self-etch adhesive systems were used in this study of which five were photo-polymerized and four dual-polymerized. For the photo-polymerized adhesive resins, fifty potassium bromide (KBr) specimens were equally divided into 10 experimental groups (n=5 per group) according to the two levels of the study; Level 1: Polymerization Protocol (the adhesive resins were photo-polymerized either at 1 mm or 10 mm from the pellet surface) and Level 2: Adhesive systems (ABU, GB, FBM+ LC, SBU LC and PU Bond).

For the dual-polymerized adhesive resins, sixty KBr specimens were divided into 12 experimental groups (n=5 per group) according to the two levels of the study; Level 1: Polymerization protocol (the adhesive resins were photo-polymerized at 1 mm from the pellet surface, 10 mm from the pellet surface or left to set chemically) and Level 2: Adhesive systems (Gr SE, FBU, FBM+ DC and SBU DC).

Application of the adhesives

All the adhesives were applied to the KBr pellets and polymerized in accordance with the manufacturer's instructions. Application procedures for the tested photo-polymerized and dual-polymerized self-etch adhesives are summarized in Tables 2 and 3, respectively.

A digital caliper (Mitutoyo, Tokyo, Japan) was used to adjust the distance between tip of the polymerization device and the pellet surface. A halogen polymerization unit (3M 2500, 3M, St. Paul, MN, USA) was used with an output of 600 mW/cm². The polymerization device was fixed on the horizontal arm of a metal stand. The removable horizontal arm was connected to a vertical arm that was attached to a base support and the distance required from the tip to the surface of the KBr pellet was adjusted. The

output of the polymerization unit was periodically controlled using a hand-held radiometer (Demetron 100, Kerr Corporation, Orange, CA, USA). The air-drying pressure was calibrated to 1 bar for gentle air-drying and 4 bar for maximum air-drying pressure using a pressure regulator connected to the air-way syringe of the dental unit.

For the photo-polymerized adhesive resins, the adhesive resins were polymerized either at 1 mm or 10 mm distance. For the dual-polymerized adhesive resins, the adhesives were photo-polymerized at either 1 mm or at 10 mm or polymerized chemically.

All KBr pellets were stored in dark containers for 24 h prior to the evaluation of the DC%.

Evaluation of the degree of conversion

Fourier Transform Infrared Spectrometer (FTIR) spectra of unpolymerized adhesive resins were obtained using 24 scans at 4 cm^{-1} in the absorbance mode (Jasco FT-IR 6400, Japan). FTIR spectra of polymerized adhesive resins were obtained after storage in dark containers for 24 h. For calculating the DC, the percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance peak areas of aliphatic carbon-carbon double bonds C=C (peak at 1637 cm^{-1}) against aromatic component (peak at 1608 cm^{-1}) which was used as an internal standard before and after polymerization. The underlying peak area was calculated for each peak, using a standard baseline technique with the aid of computer software program provided with the spectrometer (Spectra Manager Version 2).

The degree of monomer conversion was determined using the following equation:

$$DC\% = \left[1 - \frac{(1637\text{ cm}^{-1}/1608\text{ cm}^{-1})\text{ peak area after curing}}{(1637\text{ cm}^{-1}/1608\text{ cm}^{-1})\text{ peak area before curing}} \times 100 \right]$$

The DC was obtained by subtracting the percentage of remaining carbon double bonds (% C=C) from 100%.

Statistical analysis

Statistical analysis was performed using SPSS program for windows (SPSS Software Version 21, Chicago, IL, USA). For both photo-polymerized and dual-polymerized adhesives, two-Way ANOVA was used to evaluate the effect of polymerization protocol, adhesive system and their interaction on the DC%. For the photo-polymerized and dual-polymerized adhesive resins, 1-Way ANOVA followed by Tukey's HSD post hoc test were used to evaluate the effect of adhesive system within each polymerization protocol. Student t-test was used to compare the effect of distance on DC% for each adhesive resin.

Results

Two-Way ANOVA for both photo-polymerized and dual-polymerized adhesive resins showed that both polymerization protocol and adhesive system had a significant effect on the DC% of the self-etch adhesives tested in this study ($P=0.000$, respectively). The interactions between the two independent variables (polymerization protocol and adhesive system) had also a significant effect on the DC% of the both adhesive resin types ($P=0.000$).

For the photo-polymerized adhesive resins, within each polymerization protocol at 1 mm distance, there was no statistically significant difference between ABU, GB, FBM+ LC and PU Bond, which showed the highest DC% values (1-Way ANOVA, Tukey's post-hoc) (Table 4). On the other hand, SBU LC presented significantly lower DC% compared to the rest of the photo-polymerized adhesive resins. At 10 mm distance, there was no statistically significant difference between ABU, FBM+ LC, SBU LC and PU Bond and between ABU, GB, SBU LC and PU Bond. There was a statistically significant difference between GB and FBM+ LC. Student t-test revealed that the DC% values at 1 mm distance were significantly higher than at 10 mm in all photo-

polymerized adhesive resins. The average percentage drop in DC% ranged from 16.9% to 26.4% from 10 mm distance to 1 mm.

For the dual-polymerized adhesive resins, at 1 mm distance, there was a statistically significant difference between FBU/Gr SE, FBU/FBM+ DC and SBU DC/Gr SE (1-Way ANOVA, Tukey's post-hoc) (Table 5). There was however, no statistically significant difference between FBM+ DC/Gr SE, FBM+ DC/SBU DC and SBU DC/FBU. At 10 mm, FBU, FBM+ DC and Gr SE showed no statistically significant difference.

SBU DC yielded the lowest significant DC% compared to the other adhesive resins. For the self-polymerized protocol, Gr SE generated the highest significant DC% among all tested adhesives. There was no statistical significant difference between FBU and FBM+ DC that revealed the lowest DC%. The average decrease in DC% was ranged from 11.7% to 35.5%, 55.0% to 81.4% and 46.7 to 78.8% (10 mm/ 1 mm, SC/1 mm and SC/10 mm, respectively).

Discussion

Adequate radiant exposure (Irradiance x Area, joule/mm²) of resinous materials, including resin composite materials and adhesive systems, is crucial for their long-term success. The high irradiance required for optimum photo polymerization is found to be close to the tip of the polymerization unit. As this distance increases, the irradiance rapidly decreases [30,32-35]. This problem is often encountered in class II cavities, as the gingival floor of the cavity is the common site of restoration failure [36]. Appropriate light intensity should always be considered when choosing a polymerization unit so that the resin composite restoration could exhibit good clinical results [37]. A positive correlation between enhanced mechanical properties of dental restorative resins and higher DC has been elucidated [38]. On that account, the increase in the DC of dental adhesives after the prolongation of light exposure time had resulted in improved

microhardness and reduced permeability [20]. Regarding the effect of distance of light source on bond strength, it was reported that increasing the distance, had decreased the light intensity, which had negatively affected the shear bond strength of an etch-and-rinse adhesive [33]. On the contrary, Shinkai, et al. concluded that the decline in the light intensity had no effect on the shear bond strength of the tested self-etching adhesives [39]. The extent of polymerization of contemporary adhesive resin systems was found to be also dependent on the technique of solvent evaporation. One of the factors that should be considered is the evaporation time, which showed a significant effect on the DC [40].

One-step self-etch photo-polymerized adhesive resins are used routinely to bond direct resin composite material to both enamel and dentin. Meanwhile, dual-polymerized self-etch adhesives were introduced in the market to bond dual-polymerized/chemical-polymerized resin composites to enamel and dentin and fiber posts to root canal dentin. The reason why self-etch adhesive systems have been launched is to eliminate the technique sensitivity of the etch-and-rinse adhesives, decrease the clinical bonding steps and consequently shorten the chair-side time [41].

The results of photo-polymerized self-etch adhesives used in this study indicated that both factors, adhesive type and polymerization protocol, showed a significant effect on the DC. Accordingly, the first null hypothesis could be rejected. At 1 mm polymerization distance, all adhesive resins showed similar DC except the SBU LC adhesive, which revealed significantly the lowest DC. The chemical composition of SBU LC might have a major effect on the results. The dimethacrylate resins, included in this adhesive, are essential to improve its mechanical strength [42] and at the same time reduce its water sorption [43] by forming densely cross-linked polymers [42]. These cross-linkers tend to facilitate the onset of the “reaction-diffusion-controlled termination”, yet they slow down the diffusion of the reactants at later stage, which compromise the DC [42]. In addition,

bis-GMA resin is a high molecular weight resin that exhibits more rigidity during polymerization and eventually dramatically affect the DC of this adhesive [43]. The presence of polyalkenoic acid copolymer might have also played an unfavourable role by preventing monomer approximation during polymerization, due to its high molecular weight [44].

At 10 mm distance, GB adhesive demonstrated the highest DC%. In fact, reduction in distance between monomers as a result of solvent evaporation could ameliorate the conversion process [45]. Theoretically, solvent should be completely evaporated to improve the DC of the adhesive resin but complete solvent evaporation is not easy to achieve [46]. Borges, et al. concluded that none of the evaluated solvent evaporation methods had influenced the degree of conversion of acetone-based adhesives [40]. Following GB manufacturer's recommendation, the solvent was aggressively air-dried at maximum air pressure. Evaporation of the solvent using the full pressure compressed air, combined with the fact that acetone has a high vapour pressure [40,43] might have certainly led to less residual solvent within the adhesive layer. This have indeed improved the DC of the adhesive, even with increasing the distance from the light source. Furthermore, due to its higher evaporation capacity, acetone might evaporate during both the application and the polymerization of the adhesive resin, provided that no moisture contamination from the substrate surface could take place, as in the wet bonding technique [40]. As all adhesive resins were applied on dry KBr pellet surfaces, no moisture contamination was expected. This could facilitate the evaporation of the solvent from the adhesive and consequently, leaving an adhesive layer with less residual solvent. The other self-etch adhesives tested in this study showed lower DC%, but statistically comparable to GB adhesive, except the FBM+ LC, which exhibited significantly lower DC%. The remaining adhesive resins tested in this study (ABU, FBM+ LC, SBU LC and PU Bond) contain ethanol and they were air-dried using gentle

compressed air according to their manufacturer's instructions. Ethanol is known to have a lower vapour pressure compared to acetone [40,43]. Its affinity to form hydrogen bond with water or functional group in the monomer is three times more than that of acetone [40]. Likewise, HEMA is another adhesive component that potentially interferes with ethanol evaporation during the air-drying step, as it decreases the vapour pressure of the solvent and subsequently increases the adhesive viscosity [40].

All photo-polymerized self-etch adhesives exhibited generally significantly higher DC% at 1 mm distance to light source compared to 10 mm. This could be attributed to the decreased light intensity of the light source, as a consequence of increasing the distance [32,33]. It was reported that it was not possible to predict the light intensity at 10 mm distance from its measurement at 0 mm distance [36]. In the current study, this means that the linear decrease in the light intensity up to 10 mm distance of light source does not depend on its light intensity at the 1 mm distance. As previously mentioned, bis-GMA and dimethacrylate resins are the main constituents of all photo-polymerized adhesive resins evaluated in this study. Since bis-GMA is a high molecular weight resin, and dimethacrylate resins form cross-linking polymer structure [42,43], it could be hypothesized that the light intensity might be crucial for their proper polymerization. Additionally, the heat generated from the polymerization curing unit could be another way to facilitate the evaporation of the solvent, especially acetone [39]. Increasing the light distance could decrease the heat transmitted through the adhesive layer, reducing further evaporation of the solvent.

Based on the results of the DC% for the dual-polymerized self-etch adhesive resins, the second null hypothesis could be rejected. In other words, both adhesive type and polymerization protocol revealed a significant effect on the DC% of the different dual-polymerized adhesive resins used in this study. At 1 mm distance, FBU showed the lowest DC%. Both FBM+ and SBU are photo-polymerized adhesives and need to be

mixed with separate DC activator to function as dual-polymerized adhesive resins. In contrast, both FBU and Gr SE are presented to serve as dual-polymerized adhesives. The main difference between FBU and Gr SE is in the delivery form and the functional monomers included in both adhesives. FBU is launched in the market as a no-bottle system, with its DC catalyst included within the single dose delivery form, whereas, Gr SE is presented as a two-bottle system. The main function of the DC catalyst is to react with the amines of the dual-polymerized or the chemical-polymerized cement and render them more reactive to the benzoyl peroxide activator (BPO), under the acidic condition of the adhesive. In this regard, dual-polymerization mode should be used only with the materials that contain BPO activator in their compositions (FBU and FBM+ Technical information, Research and Development, VOCO GmbH, Cuxhaven, Germany). Since FBU adhesive was not mixed with its recommended resin cement, the time elapsed between the activation of the single dose and the mixing of the two liquids might have permitted the reaction between the DC catalyst with the amines within the adhesive itself. This might allow the DC catalyst to compete with the photo-initiator of the adhesive, thus impairing its DC. This explanation could be confirmed by the significantly higher DC% of FBM+. Although, FBM+ is the successor of FBU, both adhesives have the same chemical composition, but the DC catalyst of FBM+ is presented in a separate bottle. This could make such adhesive a predominately photo-polymerized adhesive with a dual-polymerization option when indicated. The presence of the DC catalyst in a separate bottle might minimize its chances of competing with the photo-initiator to react with the amines. This was clearly obvious when the FBM+ DC yielded similar DC% values (84.5 ± 1.7 and 84.5 ± 0.5 respectively) in either photo-polymerization or dual-polymerization mode.

Only the SBU DC adhesive generated significantly lowest DC% compared to all tested dual-polymerized self-etch adhesive resins, when polymerized at 10 mm distance. The

high viscosity of bis-GMA resin renders it a poorly flexible monomer [47]. The reduction in its mobility during polymerization could be attributed to the presence of the intermolecular interaction, in addition to the presence of the dimethacrylate monomers that form cross-linking polymers [42]. Moreover, the presence of sodium toluene sulfinate in the DC activator is used to boost the polymerization of the adhesive in the dual-polymerized mode by acting as an oxygen scavenger from the resin [48]. However, as the light source distance increased, the light reaching the adhesive has been attenuated. The action of the sodium toluene sulfinate most likely has become an additional obstacle in the polymerization reaction of the adhesive. When SBU was photo-polymerized without the addition of the DC activator (photo-polymerization mode) at 10 mm distance, the DC% of such adhesive did not drop to the same extent as in the case of the dual-polymerized mode at the same distance. This could justify that when SBU is used as a dual-polymerized adhesive, high light intensity is mandatory to reach an adequate DC%.

The purpose of the assessment of the DC% of the dual-polymerized self-etch adhesive resins when left to set chemically was to predict the maximum DC% that the adhesive resins could reach without the use of an external light source. As the resin composite restorations or resin cements are found in either the dual- or the chemical-polymerized form, this gives them the ability to polymerize with the dual-polymerized adhesive in the so-called “co-polymerization technique”. This technique is used commonly in bonding of fiber reinforced posts to root canal dentin. This might not represent any problem with the dual-polymerized resin composite as the light will polymerize the resin, leaving no chance for the acid-base reaction to occur between the amines in the resin composite and the acidic monomers in the adhesive. On the other hand, when chemical-polymerized resin composite is used, extended polymerization time could allow the neutralization of the amines in the resin composite with the acidic monomers of the

adhesive. In such a situation, the tertiary amines could have lost their action as reducing agents and thereby impaired the polymerization of the chemical-polymerized resin composites [49]. It was reported that when the dual-polymerized resin composite was left to set chemically over the unpolymerized dual-polymerized etch-and-rinse adhesives, the shear bond strength greatly decreased [50]. This was attributed to the high acidity of the dual-polymerized etch-and-rinse adhesive that could interfere with the chemical reaction of the resin composite. The results of the present study showed that all dual-polymerized self-etch adhesives yielded a dramatic decrease in their DC%, noting that all the adhesives do not contain BPO in their formulation. The BPO/amine system is responsible for the chemical polymerization process in resinous materials [48]. Accordingly, in the absence of BPO, the tested adhesives in this study were not able to reach their maximum DC%.

Although, there have been several controversies regarding the effect of light attenuation on bond strength [32,39], many studies have shown that the improvement in mechanical behaviour [51], decrease in water sorption and solubility [52] and reduction in the bonding interfaces permeability [20,53] were directly linked to the higher DC% of the different adhesive resins. Nevertheless, further studies should be conducted to evaluate the effect of increasing light source distance or the chemical polymerization mode of the dual-polymerized self-etch adhesives on the bond strength of both chemical- and dual-polymerized resin composites. The impact of the aforementioned variables on the water sorption and solubility of the different contemporary self-etch adhesives warrants further research.

Conclusions

From this study, the following could be concluded:

1. To attain a higher degree of conversion of the self-etching adhesive resins, the tip of the polymerization device tip should be positioned as close as possible to the adhesive layer.
2. Photo-polymerization of the dual-polymerized self-etching adhesive resins is a mandatory step to improve their degree of conversion.
3. The chemical composition of the self-etching adhesive resins has an influence on their degree of conversion.
4. It is better to place the DC catalyst/initiator in a separate bottle rather than to include it within the adhesive composition.

Clinical Relevance

In order to improve the degree of conversion of self-etch adhesive resins, the tip of the polymerization device should be placed as close as possible to the surface coated with the adhesive.

Conflict of interest

The authors did not have any commercial interest in any of the materials used in this study.

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Captions to tables:

Tables:

Table 1. The brands, abbreviations, manufacturers, chemical compositions, and batch numbers of the adhesive resins used for the experiments. MDP: methacryloyloxydecyl dihydrogenphosphate, bis-GMA, Bisphenol A diglycidyl methacrylate, 4-MET: 4-methacryloyloxyethyl trimellitic acid, HEMA: 2-Hydroxyethyl methacrylate, HEDMA: Hydroxyethyl dimethacrylate and BHT: butylhydroxytoluene.

Table 2. Microshear (μ SBS) bond strengths (Mean \pm standard deviation) of resin composite cement on dentin after cleansing methods, maximum, minimum and Confidence Intervals (95%). Same lower-case letters in each column indicate no significant differences ($p>0.05$).

Table 3. Application procedures of dual-cure self-etch adhesives used in this study.

Table 4. Means \pm Standard Deviation for the effect of adhesive system and polymerization protocol on the degree of conversion (DC%) of photo-polymerized self-etch adhesives. The same lowercase letters within each column are not statistically significant ($p=0.05$).

Table 5. Means \pm Standard Deviation for the effect of adhesive system and polymerization protocol on the degree of conversion (DC%) of dual-polymerized self-etch adhesives. The same lowercase letters within each column and the same capital letters within each row are not statistically significant ($p=0.05$).

Tables:

Adhesive Resin/ Manufacturer	Description	Chemical Composition	Batch #
All-Bond Universal (ABU) (Bisco Inc., Schaumburg, IL, USA)	Photo-polymerized self-etch adhesive	MDP, bis-GMA, ethanol, water, initiators	#120003888
G-aenial Bond (GB) (GC, Tokyo, Japan)	Photo-polymerized self-etch adhesive	4-MET, phosphoric acid ester monomer, dimethacrylate monomers, distilled water, acetone, silicone dioxide, initiators	#1207121
Futurabond M+ (FBM+ LC) (VOCO GmbH, Cuxhaven, Germany)	Photo-polymerized self-etch adhesive	Dimethacrylates, fumed silica, acid modified methacrylates, camphorquinone, BHT, amine, ethanol, water	#1420558
Single Bond Universal (SBU LC) (3M ESPE, Seefeld, Germany)	Photo-polymerized self-etch adhesive	MDP phosphate monomer, bis-GMA, dimethacrylate resins, HEMA, Vitrebond copolymer, fillers, ethanol, water, initiators, silane	#527602
Peak Universal Bond (PU Bond) (Ultradent Products Inc., South Jordan, UT, USA)	Photo-polymerized self-etch adhesive	Bond: 2-HEMA, ethyl alcohol, methacrylic acid, chlorhexidine di(acetate)	#B8L9N
Gradia SE (Gr SE) (GC Tokyo, Japan)	Dual-polymerized self-etch adhesive	Liquid A: 4-MET, water, ethanol, dimethacrylates, silica fillers, initiator Liquid B: ethanol, initiator	#1302011 #1302011
Futurabond U (FBU) (VOCO GmbH)	Dual-polymerized self-etch adhesive	Liquid1: Dimethacrylates, fumed silica, acid modified methacrylates, camphorquinone, BHT, amine Liquid 2: Ethanol, water, DC catalyst	#1316210
Futurabond M+ (FBM+ DC) (VOCO GmbH)	Dual-polymerized self-etch adhesive	Adhesive: Dimethacrylates, fumed silica, acid modified methacrylates, camphorquinone, BHT, amine, ethanol, water DC Activator: Ethanol, water, DC catalyst	#1420558 #1430177
Single Bond Universal (SBU DC), (3M ESPE)	Dual-polymerized self-etch adhesive	Adhesive: MDP phosphate monomer, dimethacrylate resins, HEMA, Bis-GMA, Vitrebond copolymer, fillers, ethanol, water, initiators, silane DC Activator: Eodium toluene sulfinate, ethanol	#527602 #498022

Table 1. The brands, abbreviations, manufacturers, chemical compositions, and batch numbers of the adhesive resins used for the experiments. MDP: methacryloyloxydecyl dihydrogenphosphate, bis-GMA,

Bisphenol A diglycidyl methacrylate, 4-MET: 4-methacryloyloxyethyl trimellitic acid, HEMA: 2-Hydroxyethyl methacrylate, HEDMA: Hydroxyethyl dimethacrylate and BHT: butylhydroxytoluene.

Adhesive Resin	Application Procedures
ABU	1- Two separate coats of the adhesive were applied to the surface of the KBr pellet for 10-15 s each time using a micro-brush (Single Tim, VOCO GmbH, Cuxhaven, Germany) 2- Air-dried using gentle compressed oil-free air (1 bar) for 10 s 3- Photo-polymerized for 10 s
GB	1- The adhesive was applied to the KBr pellet surface using the micro-brush and left undisturbed for 10 s 2- Air-dried for 5 s under high air-drying pressure (4 bar) 3- Photo-polymerized for 10 s
FBM+LC	1- The adhesive was applied to the KBr pellet surface using the micro-brush and gently rubbed for 20 s 2- Gently air-dried (1 bar) for 5 s 3- Photo-polymerized for 10 s
SBU LC	1- The adhesive was applied to the KBr pellet surface using the micro-brush and gently rubbed for 20 s 2- Gently air-dried (1 bar) for 5 s 3- Photo-polymerized for 10 s
PU Bond	1- The PU Bond was used solely, without its self-etching primer. The adhesive was scrubbed gently for 10 s over the KBr pellet surface using the brush supplied by the manufacturer (Black Mini brush tip, Ultradent Products, Inc., South Jordan, UT, USA) 2- Gently spread over the surface for 10 s 3- Photo-polymerized for 10 s

Table 2. Application procedures of photo-polymerized self-etch adhesives used in this study.

Adhesive Resin	Application Procedures
Gr SE	1- One drop of liquid A and one drop of liquid B were mixed into a mixing palette for 5 s until a homogenous mix was obtained 2- Applied to the KBr pellet surface using the micro-brush and left undisturbed for 30 s 3- Gently air-dried for 10 s 4- Photo-polymerized for 10 s at the respective distances or left to set chemically
FBU	1- Single Dose blister was activated by pressing the blister to allow the liquid flow out into the mixing and dispensing chamber 2- The foil was punctured using the Single Tim applicator 3- The adhesive was mixed thoroughly with the applicator for 2 s until a homogenous mix was obtained 4- Applied to the KBr pellet surface and gently rubbed for 20 s 5- Gently air-dried for 5 s 6- Photo-polymerized for 10 s at the respective light curing distances or left to set chemically
FBM+ DC	1- One drop of the adhesive and one drop of the DC activator were mixed into a mixing palette for 3 s until a homogenous mix was obtained 2- Applied to the KBr pellet surface and gently rubbed for 20 s 3- Gently air-dried for 5 s 4- Photo-polymerized for 10 s at the respective distances or left to set chemically
SBU LC	1- One drop of the adhesive and one drop of the DC activator were mixed into a mixing palette for 5 s until a homogenous mix was obtained 2- Applied to the KBr pellet surface and gently rubbed for 20 s 3- Gently air-dried for 5 s 4- Photo-polymerized for 10 s at the respective distances or left to set chemically

Table 3. Application procedures of dual-cure self-etch adhesives used in this study.

	Photo-polymerization (1 mm)	Photo-polymerization (10 mm)	<i>P</i> value
ABU	82.8 ± 1.7 ^a	63.4 ± 3.6 ^{ab}	0.004
GB	82.9 ± 1.4 ^a	68.8 ± 0.7 ^a	0.001
FBM+LC	84.5 ± 1.7 ^a	62.2 ± 2.5 ^b	0.000
SBU LC	78.1 ± 0.04 ^b	62.6 ± 0.5 ^{ab}	0.000
PU Bond	84.6 ± 0.09 ^a	66.6 ± 2.8 ^{ab}	0.000

Table 4. Means ± Standard Deviation for the effect of adhesive system and polymerization protocol on the degree of conversion (DC%) of photo-polymerized self-etch adhesives. The same lowercase letters within each column are not statistically significant (p=0.05).

	Photo-polymerization (1 mm)	Photo-polymerization (10 mm)	Chemical- polymerization
FBU	79.5 ± 0.8 ^{c,A}	70.2 ± 3.4 ^{a,B}	14.8 ± 1.1 ^{c,C}
FBM+DC	84.5 ± 0.5 ^{ab,A}	68.0 ± 0.3 ^{a,B}	19.0 ± 1.5 ^{c,C}
Gr SE	86.0 ± 1.5 ^{a,A}	73.0 ± 3.9 ^{a,B}	38.7 ± 3.5 ^{a,C}
SBU DC	82.2 ± 1.4 ^{bc,A}	53.2 ± 3.9 ^{b,B}	28.3 ± 1.2 ^{b,C}

Table 5. Means ± Standard Deviation for the effect of adhesive system and polymerization protocol on the degree of conversion (DC%) of dual-polymerized self-etch adhesives. The same lowercase letters within each column and the same capital letters within each row are not statistically significant (p=0.05).